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ISTITUTO ELETTROTECNICO NAZIONALE GALILEO FERRARIS

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SUMMARY
~~FINAL~~ REPORT - Part B. January 1962

CONTRACT : AF 61 (052)-328.

OBJECTIVE OF THE WORK : Experiments on Electroluminescence.

AUTHORS : G.Bonfiglioli, P.Brovetto, R.Malvano.

TITLE : " On the relation between Frozen Polarization and Electroluminescence of ZnS Cells."

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SUMMARY: The kinetics of the decay of the Frozen Polarization (FP) shown by an Electroluminescent Cell (ELC) after excitation which a suitable waveform of electrical potential has been studied as a function of temperature between + 7°C and + 42.5°C. The order of the kinetics has been evaluated as well as the thermal activation energy, which turned out to be around 2.5 eV. This figure corresponds closely to the ionization energy of Cu^+ impurities in ZnS(Cu) phosphor. Independently we investigated the kinetics of the decay of the amount of light which an ELC gives out, under excitation by a single linear voltage transient retarded on variable amounts with respect to a previous excitation. The latter consisted of a train of linear transients long enough to "saturate" the cell. The phenomenon has been followed from -44.5°C to + 47.5°C and again an activation energy has been found of roughly 1.5 eV. The connection between these two experiments and its possible implications are briefly discussed, in the attempt to cast some light on the mechanism of barrier injection of carriers in EL phosphors.

1) - INTRODUCTION.

The fact that a ZnS ELC (of the condenser type), after excitation with ac or any other suitable waveform of electrical potential behaves somewhat like an "electret", that is remains charged even if its electrodes are short circuited is well known. This amounts to say that a polarization has been originated within the cell, and has been "frozen in" through some mechanism - although as experiment tells, in a more or less long time the charge decays away. In footnote (1) we quote only some of the papers dealing with this subject, even though the literature is actually rather abundant. Among the papers quoted,(1d) looks particularly interesting from our point of view - in the sense the Authors have attemped to put into very close correspondence the behaviour of the FP and the "ability" of the cell to give out a definite amount of light if excited in a certain way. More precisely the quoted Authors have measured the FP of an ELC of the condenser type, with the technique of the Volta movable plate condenser. The measurement was performed(apparently) at room temperature, and the behaviour of the FP was followed vs. time, what showed a monotonically decreasing curve.

Independently, a measurement of "integrated light output" was performed, for the details of which the reader should refer to the original paper spoken of. We are interested here in the fact that the behaviour of such a light output was followed as a function of the time elapsed by a previous electrical excitation undergone by the ELC.

This experiment therefore closely resembls in its main lines our present experiment , as the reader will be able to appreciate shortly. Waymouth and Bitter found that a same curve accounted for the behaviour vs time of both FP and integrated light output. We shall show in the following that this property does not

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(1) a) V.M.Fridkin,A.N.Bogatyrev,and E.V.Brakhman,Soviet Phys. Solid State, 2, 1952 (1961).

b) B.M.Golovin,N.T.Kashukeev,I.N.Orlov,and V.M.Fridkin, Soviet Phys. Solid State, 2,911 (1961).

c) J.R.Freeman,H.P.Kallman,M.Silver,Rev.Mod.Phys.,33,553(1961)

d) J.F.Waymouth,F.Bitter, Phys.Rev. 95,941 (1954).

hold generally.

Let us remark now that the theory of EL by Zalm[2], which we took as a starting point for our investigations[3], considers that the injection of carriers into the phosphor takes place by a barrier mechanism and therefore suggests in some way a relation between luminous output and FP. Moreover, the most trivial experimental evidence shows that a previously strongly excited cell(let us call it a "pumped" ELC) is much more able to glow under a further potential pulse than an unpumped one. And actually a pumped cell is always strongly polarized. It is evident however that these facts do not suffice by themselves to authorize the statement that FP is the "cause" of the light output , nor that these quantities are connected to each other by any simple functional relationship - although actually it could seem reasonable that it should be so.

To clarify , if possible, this important point, is the aim we had in mind when we started the experiments reported in the following.

2) - EXPERIMENTS ON FP.

The specimens used in present experiments were commercial Westinghouse Cells (Rayscent Panels) of the "green" type. The characteristics of the phosphor (ZnS:Cu,Cl) are reported in Ref. (3). The measurement of FP in such sealed cells obviously could not be performed with the technique of the Volta condenser.

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(2) P.Zalm, Phil.Res.Rep.,11, 353 and 417 (1956)

(3) G.Bonfiglioli,P.Brovetto,C.Cortese,Techn.Note No.4,Contract AF 61(052)-323.(U.S.A.F.)

We therefore made use of an Electrometer circuit , which is explained in Fig. 1 and in its caption.

The circuit operates as follows: while switch S is in position (1,1') the ELC is pumped through the telegraphic key T. Then S is rapidly switched in (2,2') and from this moment on the ELC and the auxiliary capacitor C are connected in series. The electrometer therefore measures the slowly varying difference of potential across C,which is proportional to the FP of the ELC. The "graphispot" recorder makes a record of the measurement. Needless to say, the capacitor C should be of very good quality, its insulation must correspond to a time constant much greater than the duration of the experiment, and primarily it must not show the slightest after effect of polarization which clearly would severely interfere with the measurement. These requirements have been satisfactory met by a polystyrene capacitor.

The measurements have been carried out at various temperatures, namely: 23;29;31.5;33.9;36.2;38;39;42.5 °C. For this , the ELC has been fastened to the (copper) bottom of a demountable glass Dewar flask, wrapped in black "scotch tape" to keep the cell in darkness. A resistance thermometer was placed in contact with the cell, and the hollow part of the Dewar was filled with water in which an helix of lead tube was immersed, supplied with oil coming from an ultrathermostat , to get a very accurate control of the temperature.

Fig.(2 a and b)shows, as an example, two records of the polarization decay. It proved practically impossible to perform the measurements in a wider range of temperatures, since the record at higher temperatures becomes suddendly too short or, alternatively, exceedingly long at lower temperatures.

From the records of the polarization P(t), through graphic derivation, curves of dP/dt were drawn and finally log P(t) vs logdP/dt plottings were obtained that gave , through equation $-dP/dt= K(T)P^{\alpha}$ the order α of the kinetics.These plottings are shown in Fig. 3 (a,b;c;d;e;f;g;h) and turned out to be straight lines or broken straight lines - with sufficient accuracy.

As can be seen, 2^{d} order kinetics was noticed between 28 and 31.5 °C. At higher temperatures, from 33.9 up to 42.5, two different kinetics appear, the decay beginning with 2^{d} order and ending with 1^{st} order.

Some attempt at lower temperatures, like + 7°C, gave higher order kinetics, between 3 and 4 (Cfr. for example Fig. 4).
At least tentatively,we shall not consider as significant such results which we are inclined to attribute to unknown but spurious effects. We cannot at present give any thorough justification of this working hypothesis - which is made only because the general picture of the phenomena is very much involved. At most, one can think that any "spurious" cause, if present, is likely to make the decay of P(t) faster and never slowlier . Now, a "faster" decay clearly simulates a higher kinetics than the true one.

The kinetics of order 1 and 2, on the other hand, are believed to be real - as confirmed by the coincidence of their activation energies, as we shall show shortly. This, in spite of the preliminary character of present results, (that we desire to stress out): in fact, no use has been made of least squares method, derivatives have been obtained by the method of the "mirror" and not by using numerical equations, the accuracy of temperature measurements is rather scant, the temperature range is very limited , exc. We shall see that nonetheless the results obtained may be interesting.

3) - RESULTS ON FP.

The experimental points of Fig. 3 have been connected with straight lines drown by a " naked eye best fit " method, where the order of kinetics (say 2 or 1) is fixed a priori.

In this way two other curves have been obtained(they are reproduced in Fig. 5 and 6) giving the logarithm of the constants of reaction $K_1(T)$ and $K_2(T)$ as a function of $1/T$ for the two processes respectively. The activation energies we got in this way turn out to have the values:

E_1 = 2.37 eV (1^{st} order process)
E_2 = 2.44 eV (2^{d} " ")

and can be considered as coincident within the experimental error. An interesting check of the confidence to be given to these figures has been made, measuring the decay of polarization while the cell was illuminated with green light ($h\nu \simeq 2.5$ eV; $\lambda \simeq 5000$ Å): the decay took place very much faster , as shown in Fig. 7.

This result clearly strongly speaks in favour of the existance of thermally activated processes with an activation energy near to that obtained before. The green light was produced filtering with a green glass the light from a small 150 W slide projector (about 8 feet far) and passing the beam through a thick water filled cell, to be sure that no sensible warming of the sample could result.

Let us point out that, to account for the variation of the decay speed under illumination in terms of temperature, it would be necessary to accept that temperature has been increased of something like 10°C or more - what is orders of magnitude greater than the actual warming of the ELC under our experimental conditions.

Let us stress now that the E value just found is very close to the value of the ionization energy of Cu^+ ions in ZnS[4], though it cannot be excluded that this is due to a casual coincidence. An interpretation is rendered even more difficult, due to the fact that two processes , with 1^{st} and 2^{d} order kinetics respectively must be made to fit together into a unique interpretation frame. At any rate, we postpone any further comment to the discussion paragraph, passing to report about the second group of experiments.

4) - EXPERIMENTS ON THE DECAY OF THE INTEGRATED LIGHT.

We shall make free reference in the following paragraph to our previous Technical Note No. 4[3], as to the detailed description of the specimens composition, the technique of excitation through linear transients,the photomultiplier/filter/collimator setup.

Present experiments have been performed with "green" filter , a fixed maximum voltage of 200 V, a fixed rate of variation $\dot{V}$= 600 V/m sec, using rising transients only.

The "pumping" of the ELC consisted of 20 linear rising transients, followed by fallings when the microswitch was open, within a time of about 10 sec. This pumping has been proved to be sufficient for "saturation".

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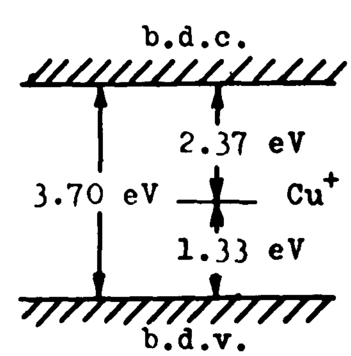
(4) A simplified scheme of energy levels of ZnS(Cu) which is generally agreed upon is the following. Cfr. for example D.Curie in Proc.Int.Conf. on Color Centers and Crystal Lumin.,Torino Sept. 1960,pg. 199,Fig.1.



The results of the experiments are shown as curves whereby the ratio $\mathcal{L}(t)/\mathcal{L}(0)$ of the area of a delayed peak of light is plotted vs. the delay time t which separates this peak from a previous peak recorded immediately after pumping.

Let us open a short parenthesis about an experimental detail: namely that pumping with sinusoidal or square waves was unsuccessfully attempted. Apparently the instantaneous phase ending the pumping action was random and this caused a bad reproducibility of the height of the pumped peaks. With our present technique , on the contrary, two pumped peaks never differed by more than 15%(in height or in area). A 20 teeth cam actuated by a small motor and operating a microswitch was made use of.

The curves spoken of were drawn using the experimental results obtained at the following temperatures: - 44.5; + 10; + 20; + 47.5 °C. The curves are shown in Fig. 8(a,b,c,d). A stainless-steel Dewar flask,with copper bottom and a lucite window was used for keeping the specimen at constant temperature . The temperature , as before, was measured by a resistance thermometer and an ultrathermostat supplied with thermostatic fluid the hollow container of the Dewar. At low temperatures, ice, or a dry ice-acetone mixture was directly put into the container.

From curves of Fig. 8 operating in the same way as in polarization experiments,bilogarithmic plottings of the function and its derivative were obtained(see Fig.9 a,b,c,d),which showed with good accuracy a kinetics order of 2. Again,at low temperatures,high order kinetics (possibly of spurious origin) were found (see Fig. 9a). An activation energy was evaluated , disregarding Fig. 9a and it turned out to be: $E_3 \simeq 1.5$ eV, definitely much lower than E_1.

We think that this result even though only of a semiquantitative character rules out the possibility that the decay of the polarization has very much to do with electroluminescence.

5) - CONCLUSIONS.

A few words first of all to justify the method followed in the analysis of the experimental curves. It is practically sure that the function P(t) or $\mathcal{L}$(t) by themselves do not obey simple kinetics equations: there are certainly present several hidden variables, obeying such simple equations, and of which P(t) and $\mathcal{L}$(t) are unknown functions. This is the cause of the variable order of kinetics found experimentally - a circumstance that always verifies itself when the kinetics of a complex phenomenon is investigated in an incomplete way. However, to make a "local" use of a kinetics equation is not objectionable as far as one only desires to separate the "net" effect of the variable T, and as far as the order in which the different kinetics appear is the same in every curve: 2^{d} order at the beginning, 1st order at the end of the record , and so on.

The results obtained are besides internally consistent, and this can be considered as a justification "a posteriori". Unfortunately, we are not able at present to give any satisfactory model capable of accounting for them. Their only significant implication, we feel, is that the polarization which can be measured under the experimental conditions met with in our work is certainly not strictly related to the behaviour of after effect or "pumping" of ELC - whatever one may like to call this phenomenon.

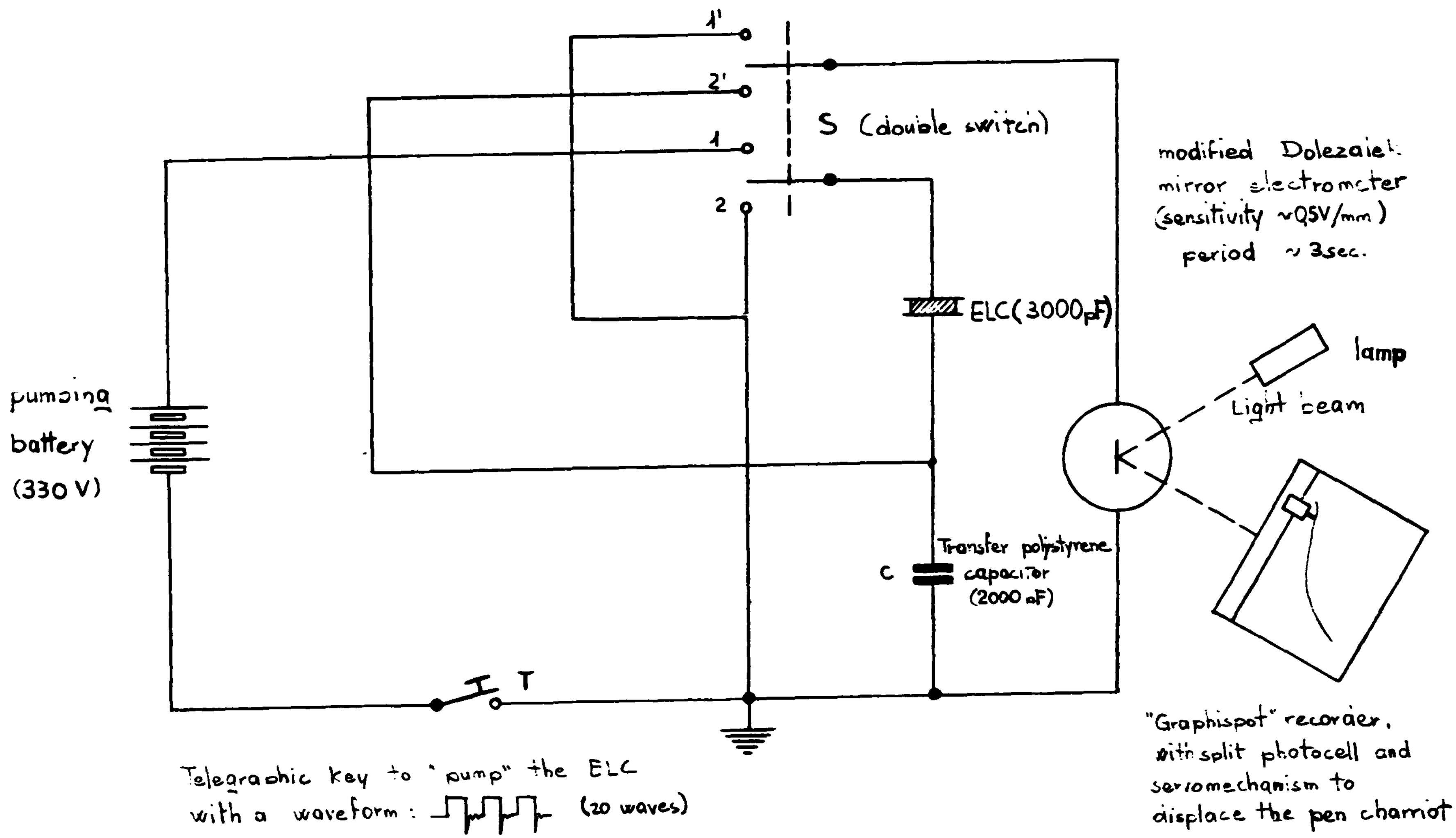
This conclusion stands on the circumstance that the behaviour vs temperature of the polarization and of the peaks of light is (strongly) different. Incidentally we observe that this important conclusion does not agree , as we pointed out in the first paragraph, with the result of Waymouth and Bitter. A possible reason can be searched in the fact that the "initial times t = 0 " , respectively for light and polarization curves of the mentioned Authors were not strictly correlated to each other , and this circumstance may be essential when one evaluates the speed of decay of a phenomenon which does not follow a first order kinetics.

We desire finally to stress out that it appears of primary importance to repete this investigation using cells formed by a monocrystalline layer of ZnS in an air(or vacuum) condenser.

This , in order to get rid of a number of trivial parameters (say, phosphor percentage, size, dielectrics properties of the binder, exc) thus simplifying in a certain measure - we hope- the interpretation problem.

We do not feel it reasonable to exclude that part of the polarization we measured , or may be a fast-decaying component not measured, can be related to an alteration of the injecting barrier, since the big phenomenon evidenced in our work could perhaps completely mask the significant one.

Let we remark that, if the hypothesis of barrier injection is correct, our second experiment gives directly a measure of the decay with time of the "penetrability" of the barrier. Perhaps this quantity ,put into correspondence with the results of a detailed calculation of barrier injection which is now in course of preparation will eventually bring out more definite conclusions.



1'
2'
1
2
S (double switch)
modified Dolezalek
mirror electrometer
(sensitivity ~0.5V/mm)
period ~3sec.
ELC(3000pF)
lamp
Light beam
pumping
battery
(330 V)
Transfer polystyrene
capacitor
(2000 pF)
C
T
"Graphispot" recorder,
with split photocell and
servomechanism to
displace the pen chariot
Telegraphic key to "pump" the ELC
with a waveform: (20 waves)

fig. 1

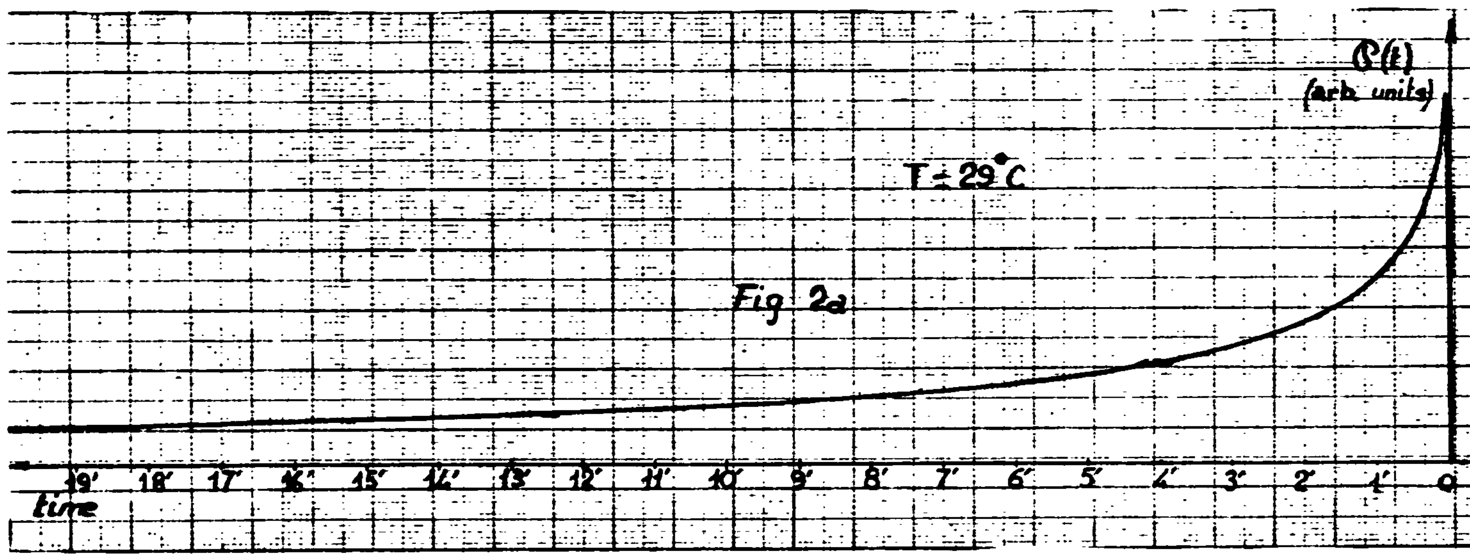

C(t)
(arb. units)
T ≐ 29°C
0 1' 2' 3' 4' 5' 6' 7' 8' 9' 10' 11' 12' 13' 14' 15' 16' 17' 18' 19'
time

Fig 2a

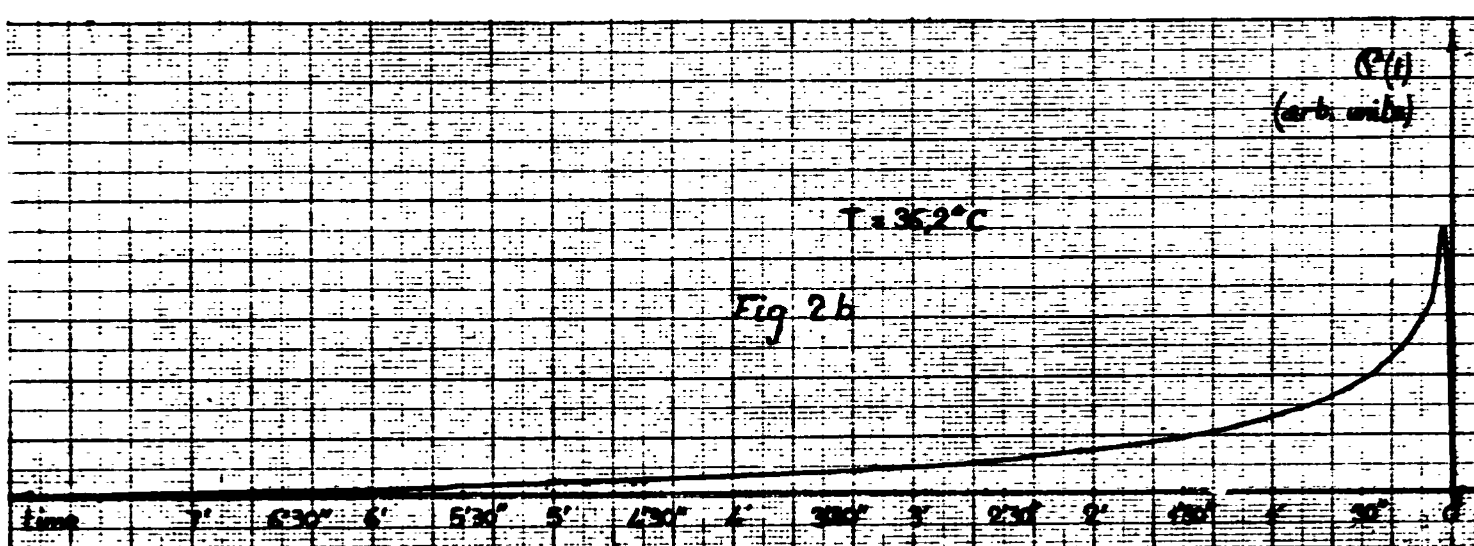
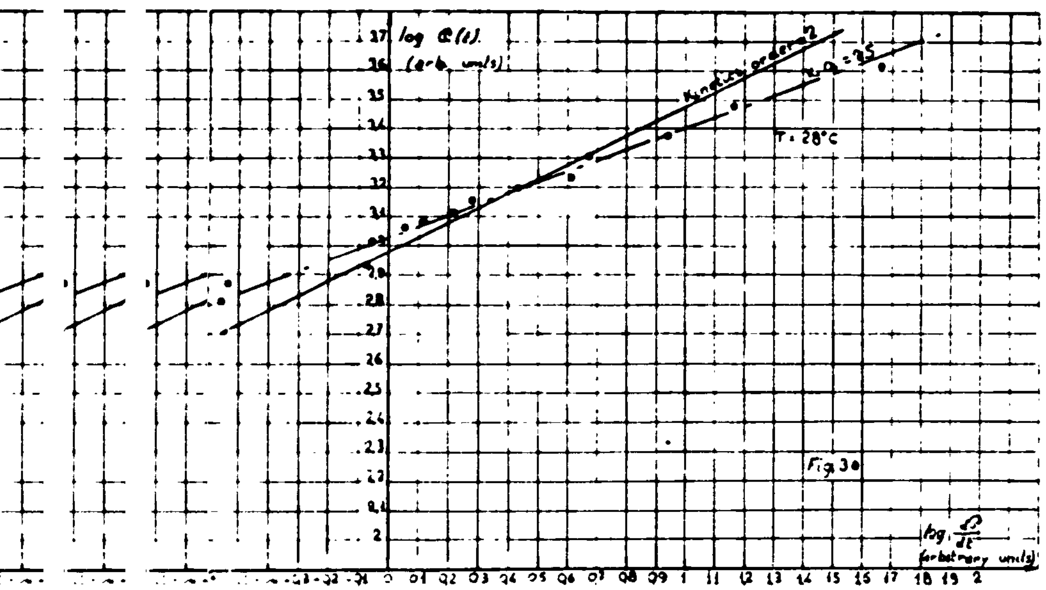
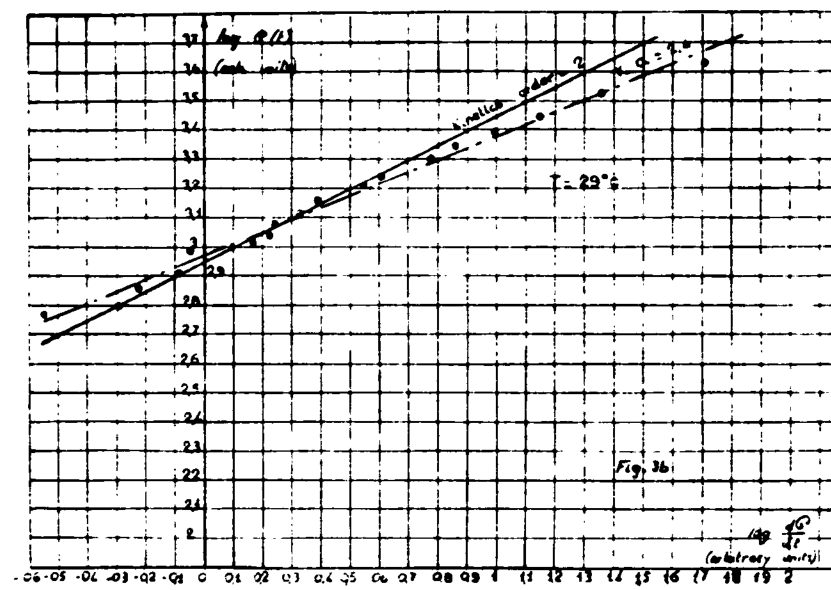
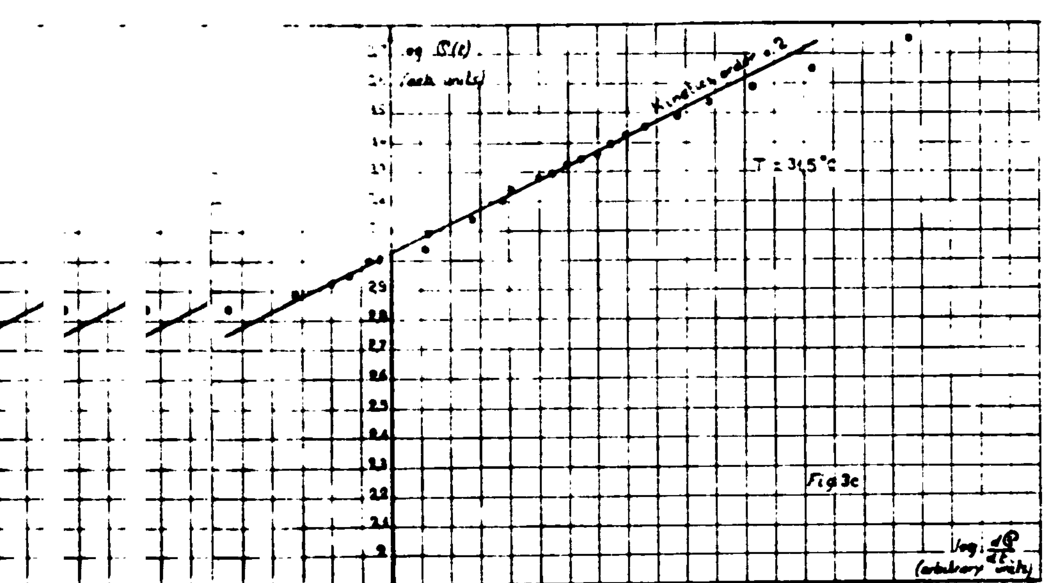
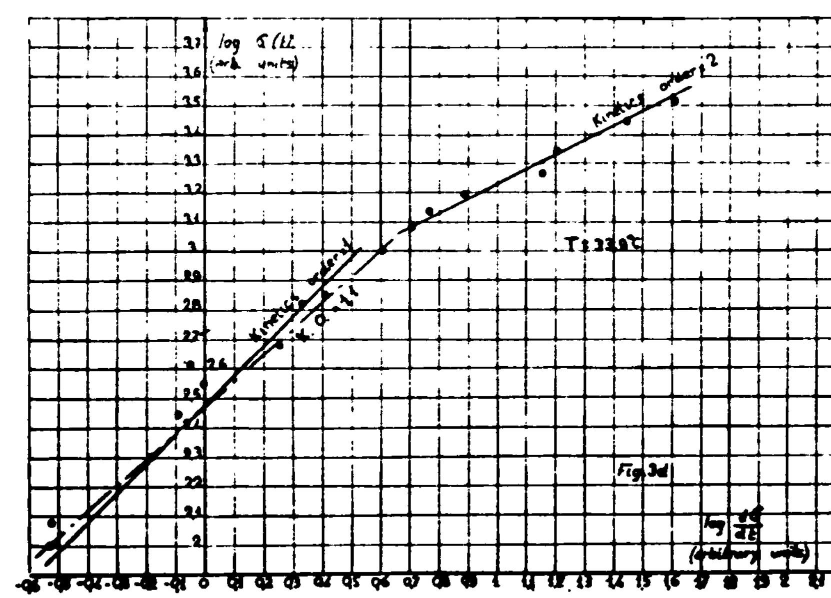

C(t)
(arb. units)
T = 36,2°C
0 30" 1' 1'30" 2' 2'30" 3' 3'30" 4' 4'30" 5' 5'30" 6' 6'30" 7'
time

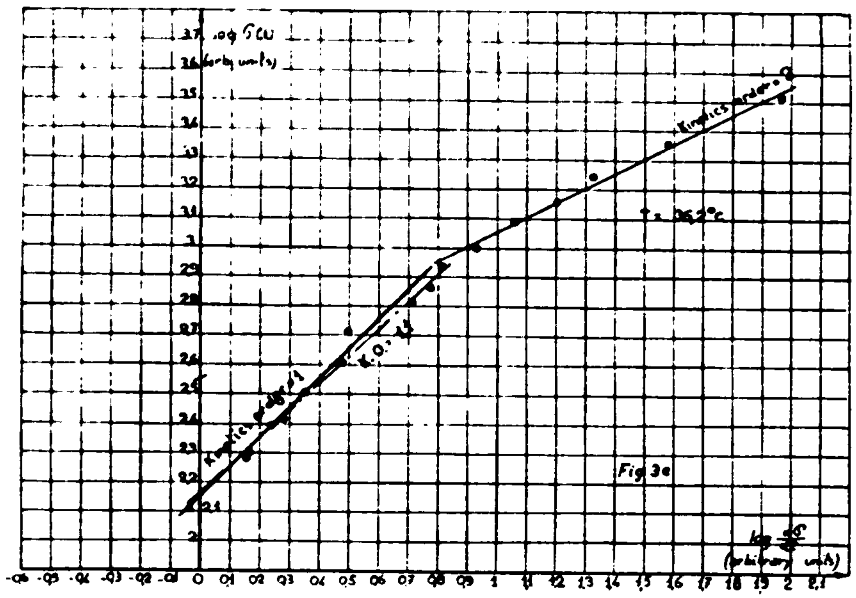
Fig 2b

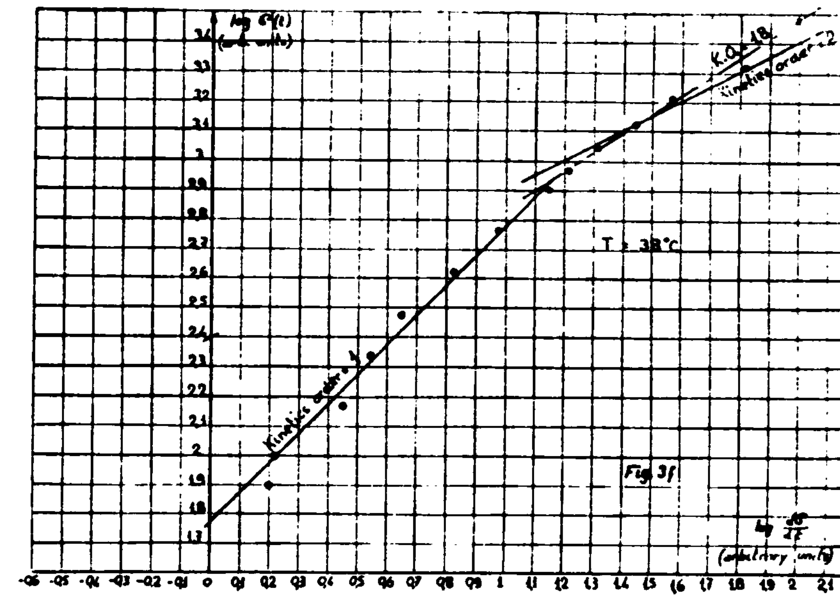

log Q(t)
(arb. units)
Kinetics order 2
T = 28°C
Fig 3a
log dQ/dt
(arbitrary units)

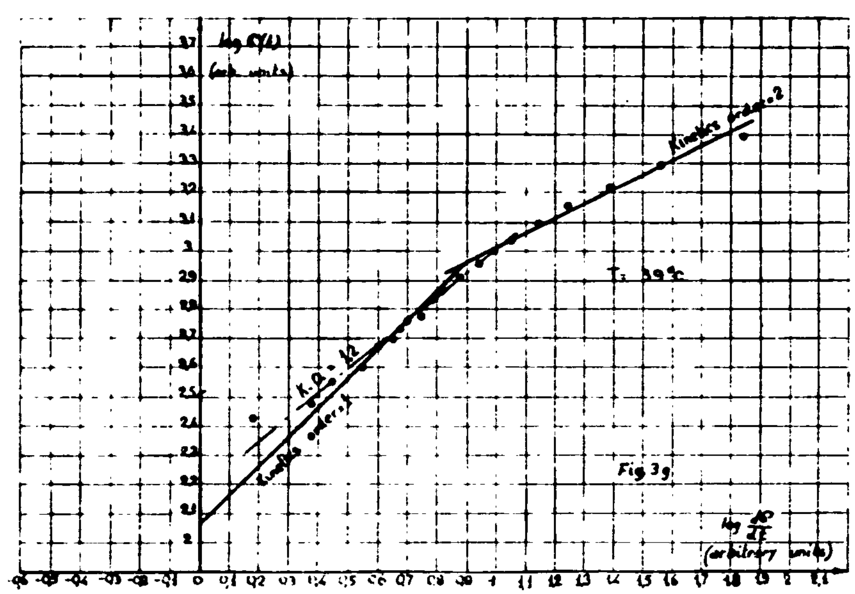

log Q(t)
(arb. units)
Kinetics order 2
T = 29°C
Fig 3b
log dQ/dt
(arbitrary units)

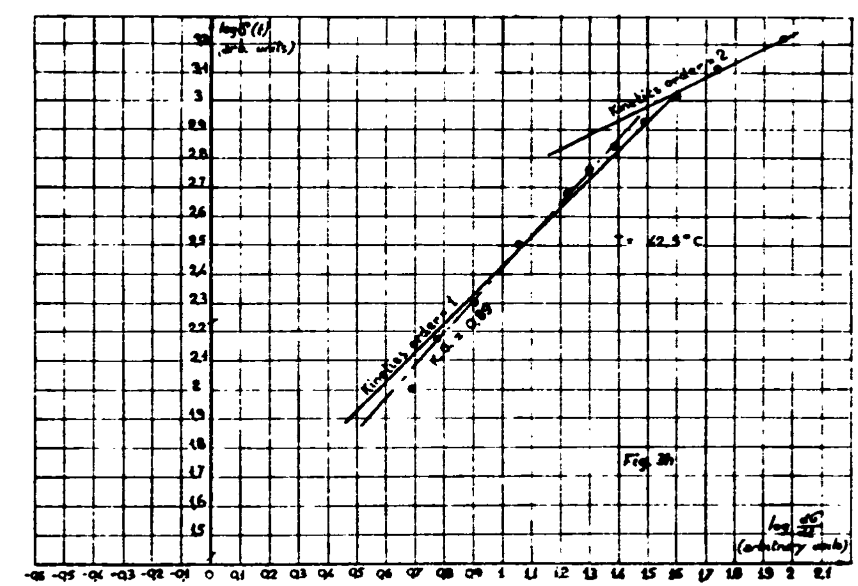

log S(t)
(arb. units)
Kinetics order 2
T = 31.5°C
Fig 3c
log dQ/dt
(arbitrary units)

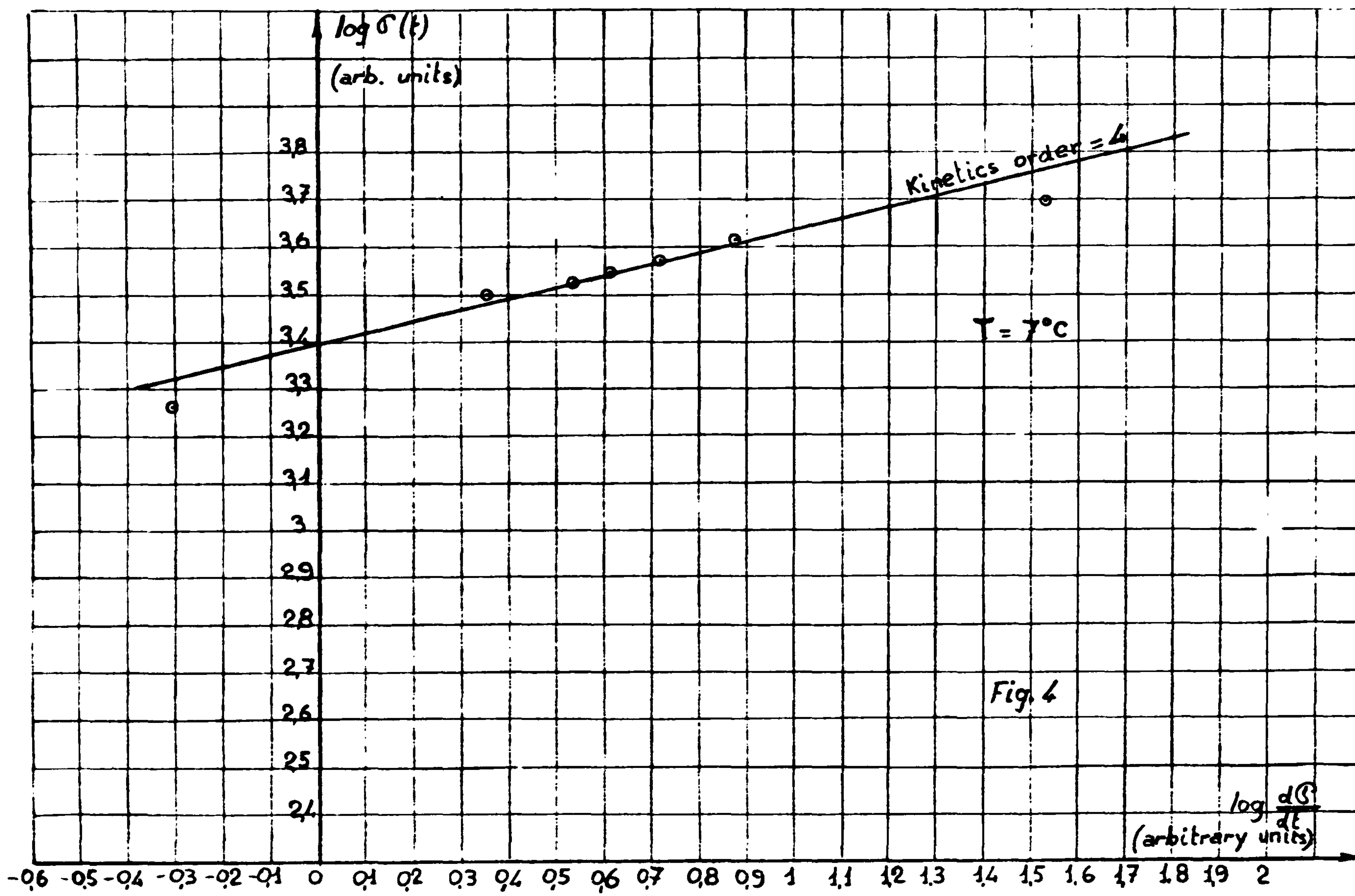

log S(t)
(arb. units)
Kinetics order 2
Kinetics order 1
T = 33.8°C
Fig 3d
log dQ/dt
(arbitrary units)


log σ(t) (arb. units)
Kinetics order = 2
T = 36.2°C
K.O. = 1.3
Kinetics order = 1
Fig 3e
log dσ/dt (arbitrary units)


log σ(t) (arb. units)
K.O. = 1.8
Kinetics order = 2
T = 38°C
Kinetics order = 1
Fig 3f
log dσ/dt (arbitrary units)


log σ(t) (arb. units)
Kinetics order = 2
T = 39°C
K.O. = 1.2
Kinetics order = 1
Fig 3g
log dσ/dt (arbitrary units)


log σ(t) (arb. units)
Kinetics order = 2
T = 42.5°C
Kinetics order = 1
K.O. = 0.89
Fig 3h
log dσ/dt (arbitrary units)


log σ(t)
(arb. units)
Kinetics order = 4
T = 7°C
log dσ/dt
(arbitrary units)
Fig. 4

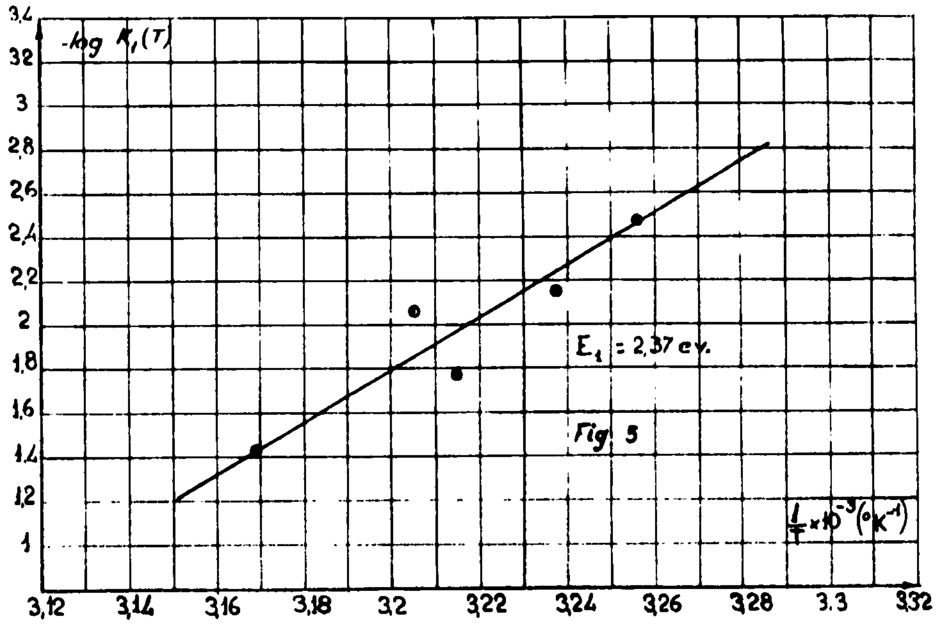

-log $K_1(T)$
3,4
3,2
3
2,8
2,6
2,4
2,2
2
1,8
1,6
1,4
1,2
1
E_1 = 2,37 ev.
$\frac{1}{T}\times 10^{-3}$ (°K^{-1})
3,12
3,14
3,16
3,18
3,2
3,22
3,24
3,26
3,28
3,3
3,32

Fig. 5

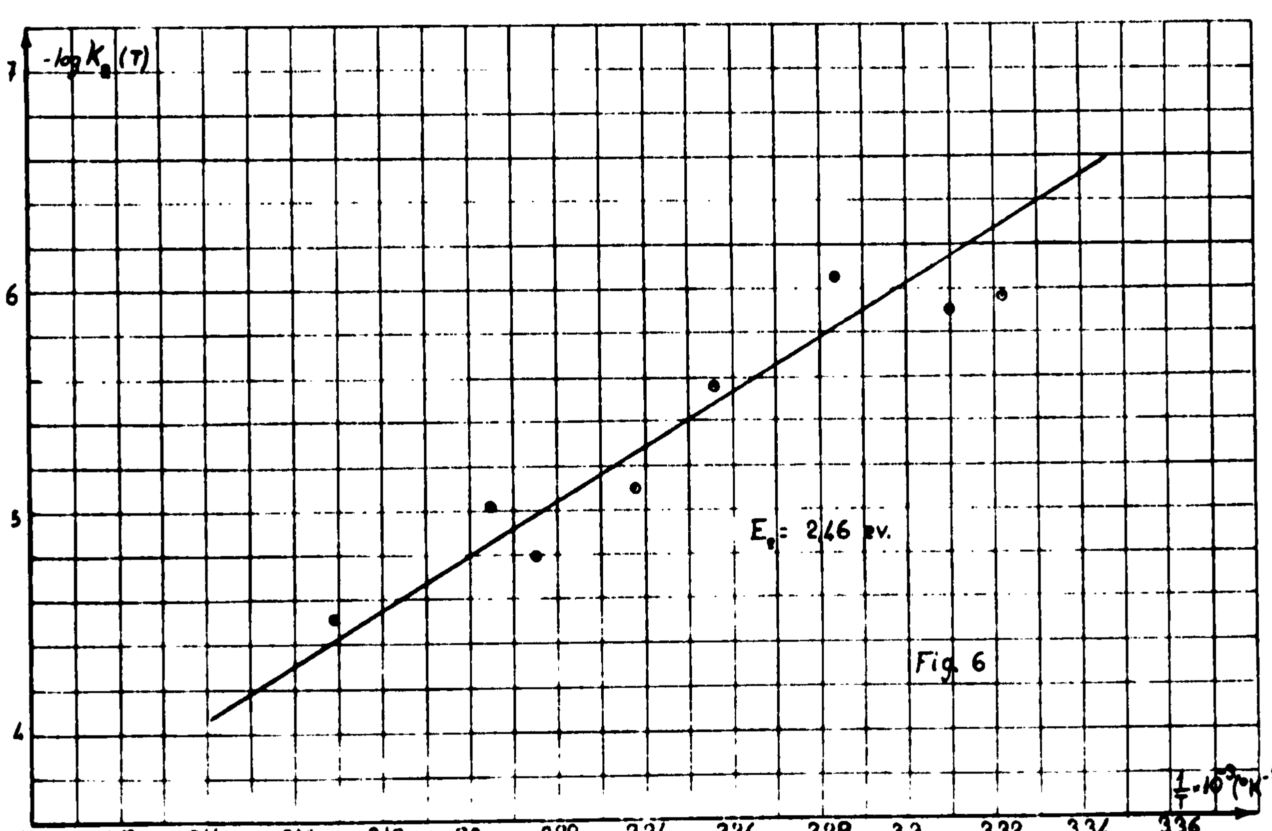
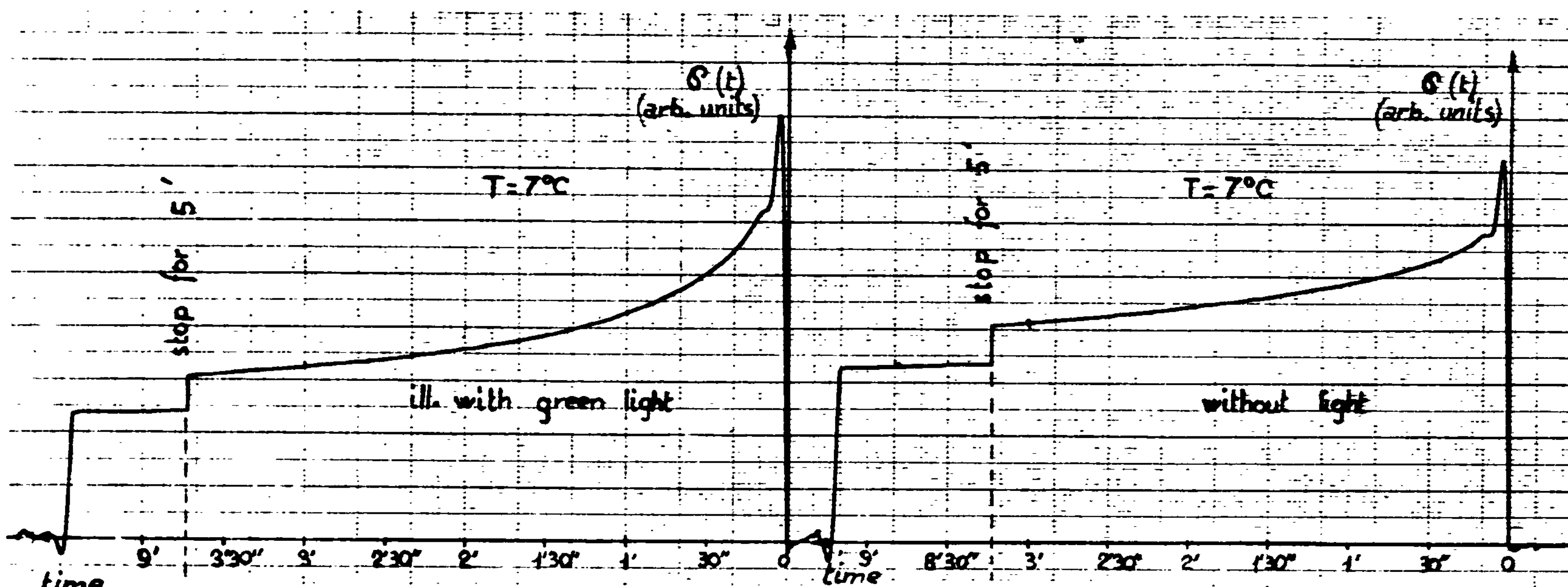

-log $K_2(T)$
7
6
5
4
E_2 = 2,46 ev.
$\frac{1}{T}\cdot 10^{-3}$ (°K^{-1})
3,1
3,12
3,14
3,16
3,18
3,2
3,22
3,24
3,26
3,28
3,3
3,32
3,34
3,36

Fig. 6



σ(t)
(arb. units)
T=7°C
stop for 5'
ill. with green light
time
9'
3'30"
3'
2'30"
2'
1'30"
1'
30"
0
σ(t)
(arb. units)
T=7°C
stop for 5'
without light
time
9'
8'30"
3'
2'30"
2'
1'30"
1'
30"
0

Fig. 7

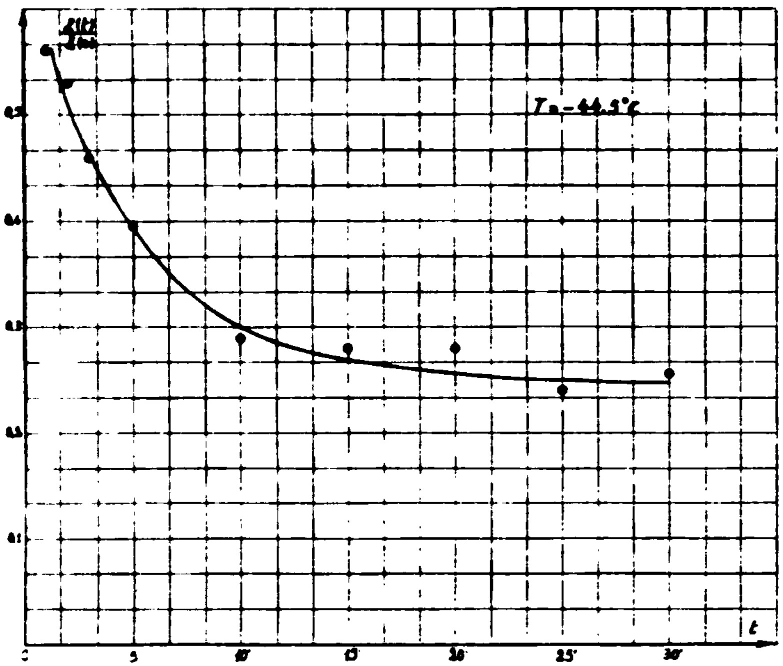


Fig. 8 - a

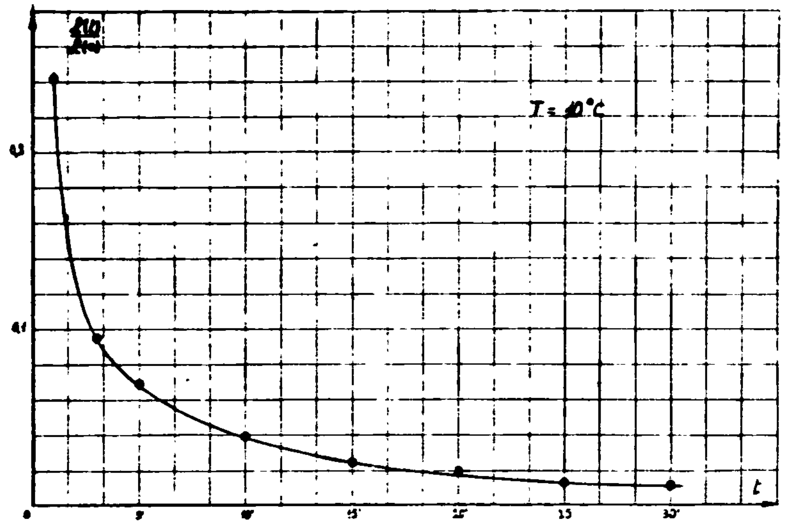


Fig. 8 - b

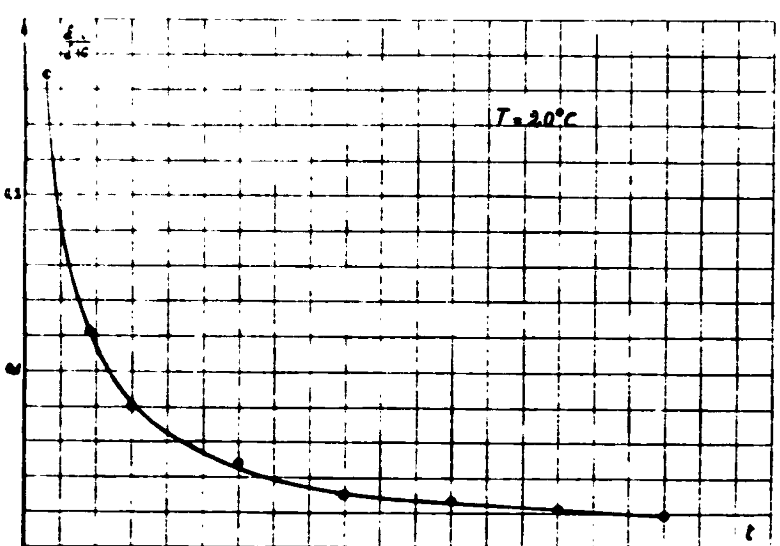


Fig. 8 - c

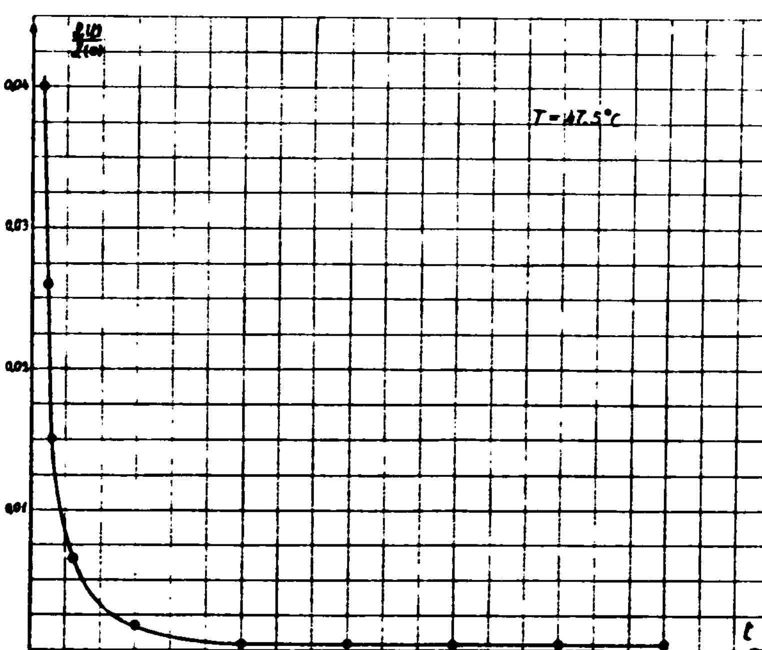


Fig. 8 - d

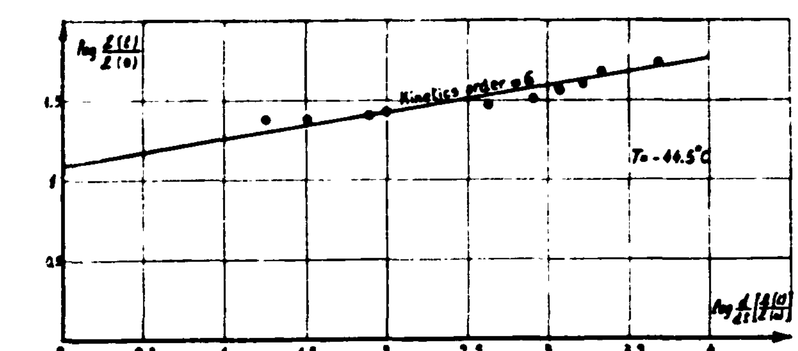


Fig. 9-a

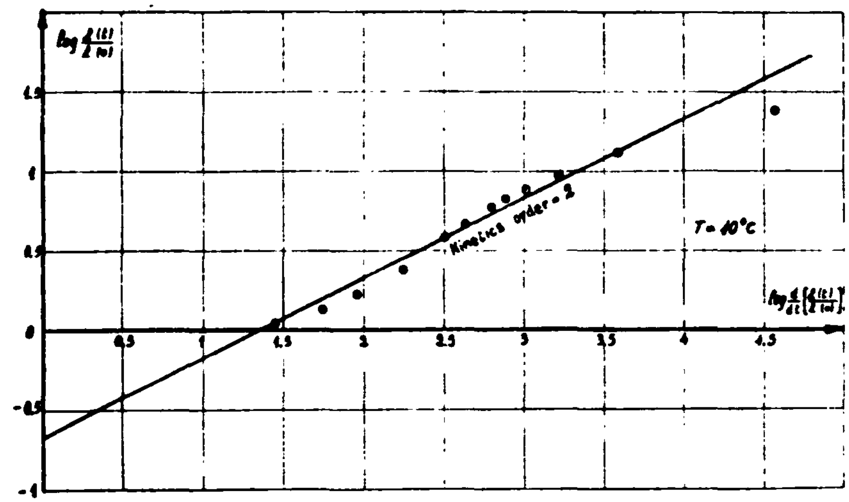


Fig. 9-b

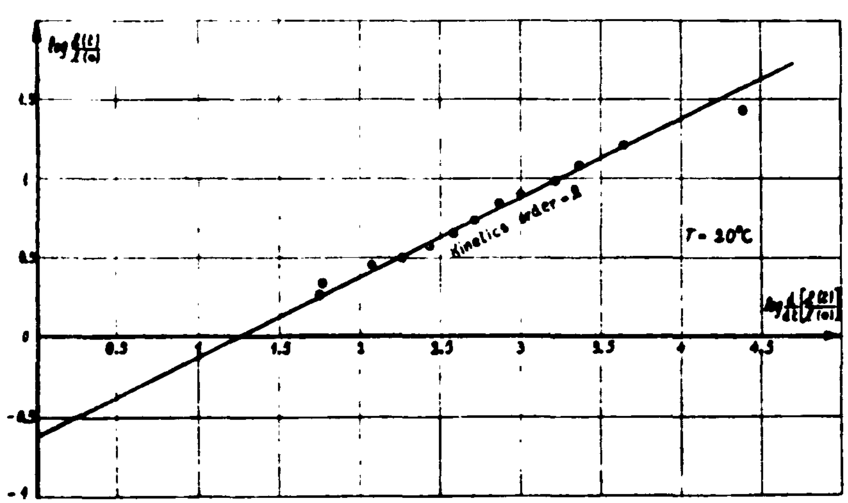


Fig. 9-c

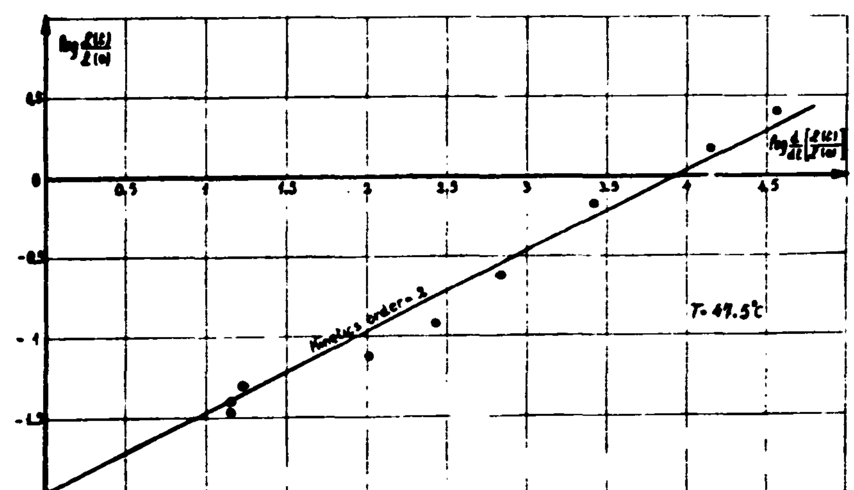


Fig. 9-d

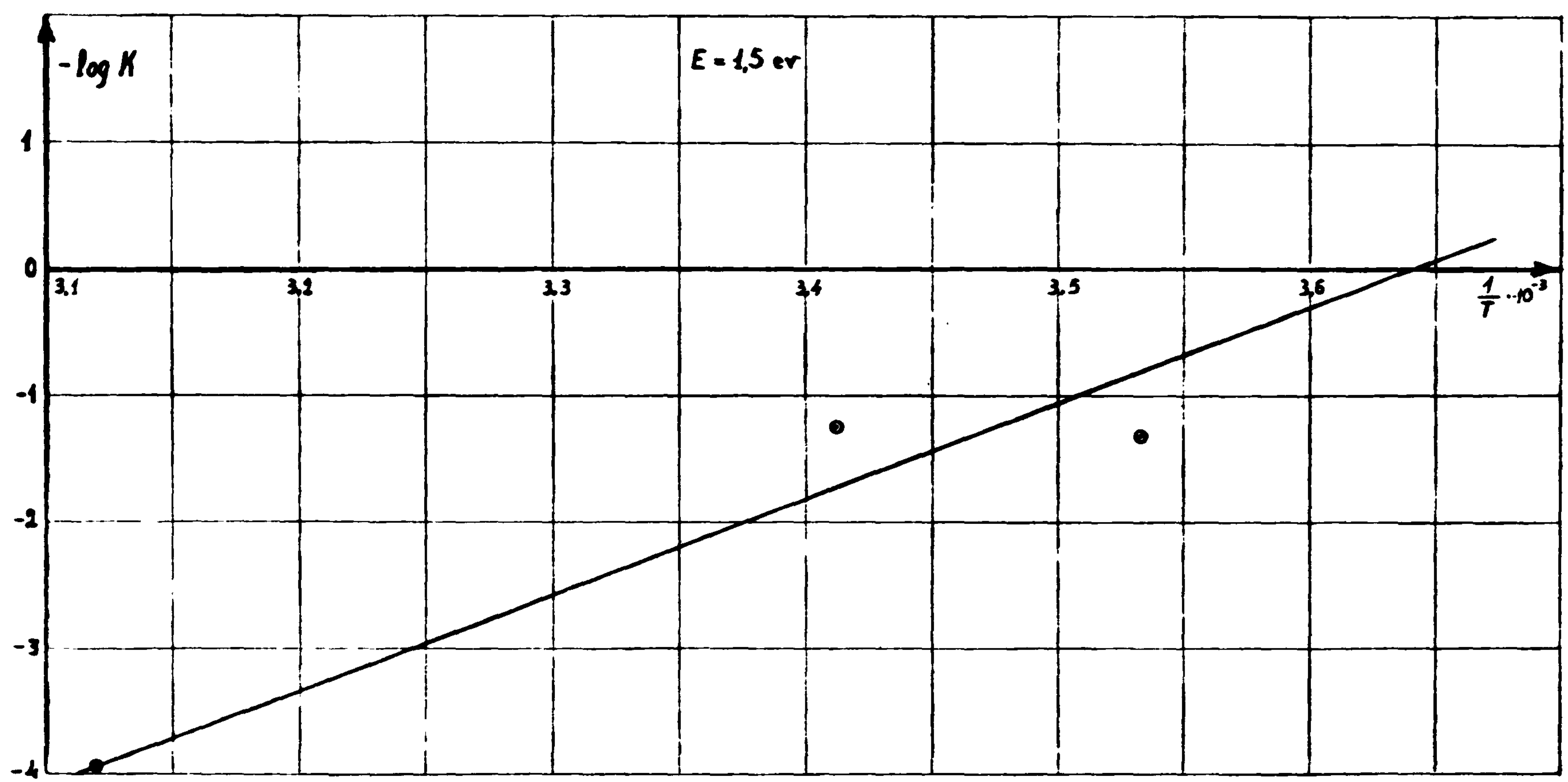


Fig. 10